

at least one monoacrylic monomer and at least one multi-acrylic monomer wherein the concentration of the monoacrylic monomer is from 0.12 to 0.90 parts by weight that of the multiacrylic monomer and wherein the ratio of the weight of the epoxy resins to that of the acrylic monomers is between 3 to 10; and

b) a combination of a free radical initiator and a photo-generating acid precursor characterized by optical molar extinction coefficients and optimized for use with a multi-wavelength argon ion laser operating in the UV and producing two major wavelengths of 351 nm and 364 nm such that a normalized ratio of the extinction coefficients of the precursor and the initiator at one major wavelength is less than 3 times the ratio of extinction coefficient at a second major wavelength.

2. (Amended) A method for accurately fabricating an integral three dimensional article having improved green strength by controlling the diffusion of photoactivated molecular species in the regions of a photohardenable liquid composition exposed to actinic radiation, the method comprising the steps of:

- (a) forming a layer of the photohardenable liquid composition;
- (b) imagewise exposing areas of at least a portion of the layers to actinic radiation at wavelengths of 351 nm and 364 nm;
- (c) introducing a new layer of liquid on to the layer previously exposed imagewise in step (b);
- (d) imagewise exposing at least a portion of the new liquid layer to actinic radiation, wherein the improvement comprises use of photohardenable liquid composition comprising:
 - a) a mixture of photopolymerizable resins consisting essentially of at least two epoxy resins, said at least two epoxy resins [one of which polymerizes] including a first epoxy resin polymerizing at a slower rate and [has] having a higher neat viscosity than at least one other epoxy resin present, [and the] said first epoxy resin[s] [are] being present at a concentration in the mixture of from 5 to 25% by weight, and

at least one monoacrylic monomer and at least one multi-acrylic monomer wherein the concentration of the monoacrylic monomer is from 0.12 to 0.90 parts by weight that of the multiacrylic monomer and wherein the ratio of the weight of the epoxy resins to that of the acrylic monomers is between 3 to 10; and

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b) a combination of a free radical initiator and a photo-generating acid precursor characterized by optical molar extinction coefficients and optimized for use with a multi-wavelength argon ion laser operating in the UV and producing two major wavelengths of 351 nm and 364 nm such that a normalized ratio of the extinction coefficients of the precursor and the initiator at one major wavelength is less than 3 times the ratio of extinction coefficient at a second major wavelength.

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3. A photohardenable composition comprising:

- (i) a mixture of cationically polymerizable components having at least two epoxy resins, said at least two epoxy resins including a first epoxy resin polymerizing at a slower rate and having a higher neat viscosity than at least one other epoxy resin present,
- (ii) a blend of radically polymerizable components;
- (iii) at least one photo-generating acid precursor;
- (iv) at least one free radical initiator; and
- (v) water;

wherein said first epoxy resin has a viscosity of greater than 1000 poise @ 25°C and a viscosity of greater than 200 poise @ 52°C.

4. The composition of claim 3 wherein said first epoxy resin has a softening point below 40°C.

5. The composition of claim 3 wherein said mixture of cationically polymerizable components comprises, relative to the total weight of said at least two epoxy resins, from 5 to 25% by weight of said first epoxy resin.

6. The composition of claim 3 wherein said blend includes at least one mono-acrylate monomer and at least one multi-acrylate monomer.

7. The composition of claim 6 wherein the total amount of mono-acrylate monomers to the total amount of multi-acrylate monomers present in the composition, on a parts by weight basis, is 0.12-0.9 parts of mono-acrylate monomers to 1 part of multi-acrylate monomers.

8. The composition of claim 6 wherein the total amount of mono-acrylate monomers to the total amount of multi-acrylate monomers present in the composition, on a parts by weight basis, is 0.27-0.58 parts of mono-acrylate monomers to 1 part of multi-acrylate monomers.

9. The composition of claim 6 wherein said at least one multi-acrylate monomer includes at least one tri-acrylate monomer.

10. The composition of claim 9 wherein the total amount of mono-acrylate monomers to the total amount of tri-acrylate monomers present in the composition, on a parts by weight basis, is 0.12-0.9 parts of mono-acrylate monomers to 1 part of tri-acrylate monomers.

11. The composition of claim 9 wherein the total amount of mono-acrylate monomers to the total amount of tri-acrylate monomers present in the composition, on a parts by weight basis, is 0.27-0.58 parts of mono-acrylate monomers to 1 part of tri-acrylate monomers.

12. The composition of claim 3, wherein the ratio, on a parts by weight basis, of said mixture of cationically polymerizable components to said blend of radically polymerizable components is from 3-10 parts of said mixture to 1 part of said blend.

13. The composition of claim 3 wherein said first epoxy resin includes an epoxy phenolic novolac resin and/or an epoxy cresol novolac resin.

14. The composition of claim 13 wherein said epoxy phenolic novolac resin has on average 3.6 or more epoxy groups.

15. The composition of claim 3 wherein said at least one other epoxy resin includes at least one cycloaliphatic epoxy.

16. The composition of claim 3 wherein said composition further comprises a sensitizer for the photo-generating acid precursor.

17. The composition of claim 3 wherein said blend of radically polymerizable components includes tetrahydrofurfuryl acrylate, isobornyl acrylate, lauryl acrylate and/or caprolactone acrylate.

18. The composition of claim 3 wherein said blend of radically polymerizable components includes caprolactone acrylate.

19. A photohardenable composition comprising:

a mixture of at least two epoxy resins wherein a first epoxy resin polymerizes at a slower rate and has a higher neat viscosity than a second epoxy resin,

at least one mono-acrylate monomer and at least one multi-acrylate monomer,

a photo-generating acid precursor,

a free radical polymerization initiator, and

water;

wherein said first epoxy resin comprises an epoxy phenolic novolac resin and/or an epoxy cresol novolac resin.

20. The photohardenable composition of claim 19 wherein the total amount of mono-acrylate monomers to the total multi- acrylate monomers present in the composition, on a parts by weight basis, is 0.12-0.9 parts of mono-acrylate monomers to 1 part of multi-acrylate monomers.

21. The photohardenable composition of claim 19 wherein the total amount of mono-acrylate monomers to the total amount of multi- acrylate monomers present in the composition, on a parts by weight basis, is 0.27-0.58 parts of mono-acrylate monomers to 1 part of multi-acrylate monomers.

22. The photohardenable composition of claim 19 wherein the ratio, on a parts by weight basis, of said mixture to said mono-acrylate and multi-acrylate monomers is from 3-10 parts of said mixture to 1 part of said mono-acrylate and multi-acrylate monomers.

23. The photohardenable composition of claim 19 wherein said epoxy phenolic novolac resin has on average 3.6 or more epoxy groups.

24. The photohardenable composition of claim 19 wherein said second epoxy resin comprises at least one cycloaliphatic epoxy.

25. The photohardenable composition of claim 19 wherein said composition comprises a tri-acrylate monomer.

26. The photohardenable composition of claim 19 wherein said at least one mono-acrylate monomer includes tetrahydrofurfuryl acrylate, isobornyl acrylate, lauryl acrylate and/or caprolactone acrylate.

27. The photohardenable composition of claim 19 wherein said at least one mono-acrylate monomer includes caprolactone acrylate.

28. The photohardenable composition of claim 19 wherein said composition further comprises a sensitizer for the photo-generating acid precursor.

29. A method for fabricating a three-dimensional article comprising:

a. forming a layer of a photohardenable composition comprising,

- (1) a mixture of cationically polymerizable components having at least two epoxy resins, said at least two epoxy resins including a first epoxy resin polymerizing at a slower rate and having a higher neat viscosity than at least one other epoxy resin present,
- (2) a blend of at least one mono-acrylate monomer and at least one multi-acrylate monomer;
- (3) at least one photo-generating acid precursor; and

- (4) at least one free radical initiator;
- b. imagewise exposing areas of at least a portion of the layer to actinic radiation; and
- c. introducing a new layer of said composition on to the layer previously exposed imagewise in step (b) and repeating step (b).

30. The method of claim 29 wherein said first epoxy resin has a viscosity of greater than 1000 poise @ 25°C.

31. The method of claim 29 wherein said first epoxy resin has a viscosity of greater than 200 poise @ 52°C.

32. The method of claim 29 wherein said first epoxy resin has a softening point below 40°C.

33. The method of claim 29 wherein said mixture of cationically polymerizable components comprises, relative to the total weight of said at least two epoxy resins, from 5 to 25% by weight of said first epoxy resin.

34. The method of claim 29 wherein said first epoxy resin has a viscosity of greater than 1000 poise @ 25°C.

35. The method of claim 29 wherein the total amount of mono-acrylate monomers to the total amount of multi-acrylate monomers present in the composition, on a parts by weight, is 0.12-0.9 parts of mono-acrylate monomers to 1 part of multi-acrylate monomers.

36. The method of claim 29 wherein the total amount of mono-acrylate monomers to the total amount of multi-acrylate monomers present in the composition, on a parts by weight basis, is 0.27-0.58 parts of mono-acrylate monomers to 1 part of multi-acrylate monomers.

37. The method of claim 29 wherein said blend includes at least one tri- acrylate monomer.

38. The method of claim 37 wherein the total amount of mono-acrylate monomers to the total amount of tri-acrylate monomers present in the composition, on a parts by weight basis, is 0.12-0.9 parts of mono-acrylate monomers to 1 part of tri-acrylate monomers.

39. The method of claim 37 wherein the total amount of mono-acrylate monomers to the total amount of tri-acrylate monomers present in the composition, on a parts by weight basis, is 0.27-0.58 parts of mono-acrylate monomers to 1 part of tri-acrylate monomers.

40. The method of claim 29 wherein the ratio, on a parts by weight basis, of said mixture of cationically polymerizable components to said blend is from 3-10 parts of said mixture to 1 part of said blend.

41. The method of claim 29 wherein said first epoxy resin includes an epoxy phenolic novolac resin and/or an epoxy cresol novolac resin.


42. The method of claim 41 wherein said epoxy phenolic novolac resin has on average 3.6 or more epoxy groups.

43. The method of claim 29 wherein said at least one other epoxy resin includes at least one cycloaliphatic epoxy.

44. The method of claim 41 wherein said at least one other epoxy resin includes at least one cycloaliphatic epoxy.

45. The method of claim 29 wherein said composition further comprises a sensitizer for the photo-generating acid precursor.

46. A method of forming a photohardenable composition comprising:
- a. forming a mixture of epoxy resins having a first epoxy resin which polymerizes at a slower rate and has a higher neat viscosity than a second epoxy resin, said first epoxy resin having a softening point below 40°C,
 - b. mixing in at least one monoacrylic monomer and at least one multiacrylic monomer, and
 - c. adding a photo-generating acid precursor and a free radical polymerization.

 47. The method of claim 46 further comprising admixing a sensitizer for the photo-generating acid precursor.

48. The method of claim 46 wherein said at least one multi-acrylate monomer includes a tri-acrylate monomer.

49. The method of claim 46 wherein the total amount of mono-acrylate monomers to the total amount of multi-acrylate monomers present in the composition, on a parts by weight basis, is 0.12-0.90 parts of mono-acrylate monomers to 1 part of multi-acrylate monomers.

50. The method of claim 46 wherein the total amount of mono-acrylate monomers to the total amount of multi-acrylate monomers present in the composition, on a parts by weight basis, is 0.27-0.58 parts of mono-acrylate monomers to 1 part of multi-acrylate monomers.

51. The method of claim 46 wherein the ratio, on a parts by weight basis, of said mixture of epoxy resins to said at least one mono-acrylate monomer and said multi-acrylate monomer is from 3-10 parts of said mixture to 1 part of said mono-acrylate and multi-acrylate monomer.

52. The method of claim 46 wherein said first epoxy resin comprises an epoxy phenolic novolac resin and/or an epoxy cresol novolac resin.

53. The method of claim 51 wherein said epoxy phenolic novolac resin has on average 3.6 or more epoxy groups.

54. The method of claim 46 wherein said second epoxy resin comprises at least one cycloaliphatic epoxy.

55. The method of claim 46 wherein said first epoxy resin has a viscosity of greater than 1000 poise @ 25°C.

56. The method of claim 46 wherein said first epoxy resin has a viscosity of greater than 200 poise @ 52°C.

57. The method of claim 46 wherein said mixture of epoxy resins comprises from 5 to 25% by weight of said first epoxy resin.

58. The method of claim 55 wherein said mixture of epoxy resins comprises from 5 to 25% by weight of said first epoxy resin.

59. A photohardenable composition comprising:

(a) a mixture of at least two epoxy resins, said at least two epoxy resins including a first epoxy resin polymerizing at a slower rate and having a higher neat viscosity than at least one other epoxy resin present, said first epoxy resin being present, relative to the total weight of said mixture, in an amount of from 5 to 25% by weight, said first epoxy resin having a viscosity of greater than 1000 poise @ 25°C and a softening point below 40°C,

(b) a blend of acrylate functional monomers comprising at least one multi-acrylate monomer and at least one mono-acrylate monomer, wherein the ratio of said at least one mono-acrylate monomer to said at least one multi-acrylate monomer, on a parts by weight basis, is 0.12-0.90 parts of mono-acrylate monomers to 1 part of multi-acrylate monomers,

(c) at least one photo-generating acid precursor, and

(d) at least one free radical initiator,

wherein the ratio, on a parts by weight basis, of said mixture of epoxy resins to said blend of acrylate functional monomers is from 3-10 parts of said mixture to 1 part of said blend.


60. A method of forming a three-dimensional article comprising:
- a. forming a layer of the composition of claim 59;
 - b. imagewise exposing areas of at least a portion of the layer to actinic radiation; and
 - c. introducing a new layer of said composition on to the layer previously exposed imagewise in step (b) and repeating step (b).
61. A method of forming the composition of claim 59 comprising:
forming said composition by combining said mixture of epoxy resins, said blend of acrylate functional monomers, said at least one photo-generating acid precursor, and said at least one free radical initiator.
62. An article formed by solid imaging the composition of claim 59.
63. The composition of claim 3, comprising, relative to the total weight of the composition, 0.2-3 wt% of said water.
64. The composition of claim 19, comprising, relative to the total weight of the composition, 0.2-3 wt% of said water.
65. The method of claim 29, wherein said composition further comprises water.
66. The method of claim 29, wherein said composition comprises, relative to the total weight of the composition, 0.2-3 wt% of water.
67. The method of claim 46, further comprising adding water to form said composition.

68. The composition of claim 59, wherein said composition further comprises water.

69. The composition of claim 59, wherein said composition comprises, relative to the total weight of the composition, 0.2-3 wt% of water.

70. An object comprising the article of claim 62.

71. A photohardenable composition comprising:

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- (i) a mixture of cationically polymerizable components having at least two epoxy resins, said at least two epoxy resins including a first epoxy resin polymerizing at a slower rate and having a higher neat viscosity than at least one other epoxy resin present,
 - (ii) a blend of radically polymerizable components;
 - (iii) at least one photo-generating acid precursor;
 - (iv) at least one free radical initiator; and
 - (v) about 0.75 wt% to 3 wt%, relative to the total weight of the composition, of water.

72. The composition of claim 71, wherein said composition comprises trimethylolpropane triacrylate.

73. A method of forming a three-dimensional article comprising:

- a. forming a layer of the composition of claim 71;
- b. imagewise exposing areas of at least a portion of the layer to actinic radiation; and
- c. introducing a new layer of said composition on to the layer previously exposed imagewise in step (b) and repeating step (b).

74. The composition of claim 71, wherein said at least one other epoxy resin includes a cycloaliphatic epoxy.

75. A method of forming a three-dimensional article comprising:

a. forming a layer of a photohardenable composition comprising

(i) a mixture of cationically polymerizable components having at least two epoxy resins, said at least two epoxy resins including a first epoxy resin polymerizing at a slower rate and having a higher neat viscosity than at least one other epoxy resin present,

(ii) a blend of radically polymerizable components;

(iii) at least one photo-generating acid precursor; and

(iv) at least one free radical initiator;

b. imagewise exposing areas of at least a portion of the layer to actinic radiation; and

c. introducing a new layer of said composition on to the layer previously exposed imagewise in step (b) and repeating step (b);

wherein said three-dimensional article is being formed at a room relative humidity above 50%.

76. The method of claim 75, wherein said composition comprises, relative to the total weight of the composition, 0.2 wt% to 3 wt% of water.

77. (New) The method of claim 75, wherein said composition comprises, relative to the total weight of the composition, about 0.75 wt% to 3 wt% of water.

REMARKS

Upon entry of this Supplemental Amendment, claims 1-77 will be pending. Relative to the Amendment submitted February 7, 2002, the instant claims differ in that:

- (i) In claim 3, the term "said high viscosity, slow curing first epoxy resin" has been replaced with "said first epoxy resin", as the Examiner suggested in paragraph 11 of the outstanding Office Action.
- (ii) Claim 71 has been amended to include that the composition comprises about 0.75 wt% to 3 wt% of water. Support for this amendment can be found on, *e.g.*, page 2, line 30, in combination with page 8, line 42 of the specification.
- (iii) Previous claim 72 has been cancelled.